On the role of adsorption in photocatalysis – mechanistic insights using compound speciation towards more accurate data description

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Introduction

For most of the experimental data in photocatalysis, a first order reaction rate is considered to be appropriate to describe the degradation of compounds [1]. However, the process of photocatalysis is an interplay between adsorption and reaction (between adsorbates and surface holes or dissolved compounds with formed radicals). Hence, it can be proposed that the reaction rate expression should contain also a contribution to adsorption.

Secondly, when a protic compound is dissolved in an aqueous matrix, speciation takes place [2]. In case of charged surfaces, such as TiO_2 [3], the interaction and, hence, the adsorption will be different for the individual compound forms. A successful attempt taking into account this speciation is reported in reference [1].

This work presents a mathematical framework for the description of the individual speciation equilibria and the subsequent individual irreversible reactions in a heterogeneous system. As showcase, the experimental data for the degradation of sulforhodamine B (SRB) and the use of the earlier reported enhanced TiO_2 catalyst [3] are reported. It can be noted that visible light was used – as this light source gains more and more attention [4].

Materials and Methods

Titanium dioxide (ST-01) was modified with H_2O_2 [3], named 'AHP-ST-01'. SRB is used as model compound. Acceleration of the photocatalytic reaction was envisaged by the Addition of Fe^{3+} ion to the solution.

The adsorption S, during the so-called 'dark period' (no light) in order to establish adsorption equilibrium, is calculated according Eq. (1) and the compound distribution, in the liquid phase and on the catalyst surface, is described by Eq. (2) with $\xi = m_{cat}/V$:

$$S = \left(C_{A,0} - C_{A,l}\right) / C_{A,0} \tag{1}$$

$$1 + C_{A,l} \cdot \sum_{i=0}^{N} K_i \cdot \beta_i = \frac{\xi \cdot C_{tot}}{S \cdot C_{A,0}} \cdot C_{A,l} \cdot \sum_{i=0}^{N} K_i \cdot \beta_i \tag{2}$$

When the light source is switched on, the photocatalytic degradation takes place. This is described by Eq. (3), taking into account the reaction of the surface specimens and the compound present in the liquid phase:

$$\frac{dC_{A,l}}{dt} = -\xi \cdot \frac{C_{tot}}{1 + C_{A,l} \cdot \sum_{i=0}^{N} K_i \beta_i} \cdot \sum_{i=0}^{N} k_i K_i \beta_i \cdot C_{A,l} - k_L C_{A,l} \tag{3}$$

Eqs. (1) to (3) are used in an in-house written Excel® file to estimate the adsorption and kinetic parameters in the degradation of RSB.

Results and Discussion

Figure 1 shows the adsorption data in the pH range 1 to 5. A distinct maximal value for S, calculated via Eq. (1), is observed. Assuming a typical active site concentration of 10^{+18} mol m^{-2} [7], and the experimental BET value of 304 m^2 g^{-1}, the concentration of active sites C_{tot} is 0.51 mol kg^{-1}. Significant adsorption coefficients $K_0 = (1.90 \pm 0.18)\ 10^{-3}$ μM^{-1} and $K_1 = (2.78 \pm 0.74)\ 10^{-4}$ μM^{-1} are obtained. In line of the expectations, the SRB protonated form shows better adsorption, since the catalyst surface can be considered as a layer of hydroxyl groups and repulsion towards adsorption can be anticipated for high pH values.

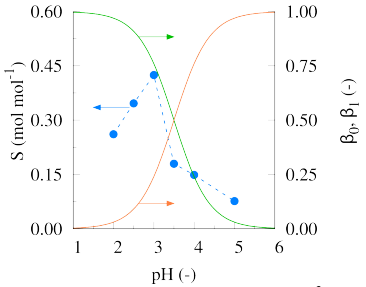

Figure 1. Experimental SRB adsorption data in AHP-ST-01-Fe^{3+} suspension (●) as function of pH and speciation values (β_0, β_1). C_{cat} = 0.50 g L^{-1}, C_{Fe3+} = 83.3 µM and $C_{SRB,0}$ = 10 µM.

Significance

The relevance of the present research is the quantitative understanding of overall photocatalytic removal processes (reaction degradation data are not presented here), which is a combination of adsorption and irreversible degradation reactions. The proposed expression (3) considers so-called 'catalyst descriptors', which can be used to screen catalysts and to make the comparison amongst each other possible from mechanistic point of view.

References

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